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Interactive comment on “In-situ submicron organic aerosol characterization at a boreal forest research station during HUMPPA-COPEC 2010 using soft and hard ionization mass spectrometry” by A. L. Vogel et al.

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Answer on Referee #1: The authors thank the referee for thorough reading and improving the manuscript by helpful comments. The manuscript will be revised based on the referee's comments as follows:

Comment 1: p.17911, line 12. It is argued that the total ACPI-MS signal as shown in Figure 1 is due to carboxylic acids. Is the contribution of other compounds classes under all conditions during this field campaign negligible?

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Reply: As it is described in chapter 2.2.1, not only organic acids can be ionized in the APCI negative mode, but also organosulfates (ROSO₃H) or nitrophenols/nitrocatechols (which are important compound classes in atmospheric chemistry) can be detected. The applied MS instrument is limited in mass resolving power, thus signals cannot be separated well enough to resolve isobaric interferences originating from organosulfates. Nitrophenols and nitrocatechols, which contain one nitrogen atom, would appear on an even-numbered m/z ratio. The measured intensity distribution between even and odd m/z values is throughout the spectrum consistent with the expected intensity distribution due to ¹³C-isotopes, and no significant signals on even m/z ratios did stand out (except for m/z 212, which unfortunately was not measured in the MS/MS mode). Furthermore, MS/MS measurements made in this study indicate the dominance of organic acids in the negative ionization mode by the neutral loss of Water and CO₂- both typical fragments of organic acids. However, it cannot strictly be ruled out that other compound classes than organic acids contribute to the measured signal. In order to be consistent with the introduction, the sentence will be rewritten as follows: “The blue time series in the top panel represents the total counts of organic acids (and possibly other compound classes such as organosulfates or nitro-phenols and catechols) in the particle phase, which is the sum of the signal intensities between m/z 150 and m/z 500, measured by APCI-IT-MS.”

Comment 2: p.17916, line 13. Figure 4 compares ambient and lab mass spectra in the range $m/z < 240$. How did the laboratory generated mass spectra compare to the ambient above this mass range? How high were the terpene concentrations in the laboratory experiments?

Reply: The intension of Fig. 4 is to show the repetitive character of an increasing oxidation state within one peak cluster. The laboratory spectrum above m/z 240 shows a range where dimers of the terpene oxidation products appear – this was published earlier (Hoffmann et al., Spectrochimca Acta, 2002; Gao et al. EST, 2010) and would draw the attention of the reader away from the central message of the figure. The

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terpene concentrations in the laboratory were ~ 200 ppb, determined by differential weighing of the diffusion source. The first sentence in chapter 2.3.1 gives now this information.

Comment 3: p. 17916, line 23. The pattern of the mass spectrum of the gas phase is less clearly spaced as the mass spectrum of the particle phase. How is this interpreted?

Reply: The fact that $\Delta m/z$ between the highest peaks in the gas-phase (171, 183, 199, 215, 229) is not always 14 Da as it is true for the particle phase (173, 187, 201, 215, 229) is an interesting observation. We assume that the amount of different monoterpene precursors have significant influence of the peak heights, since the laboratory study (lower panel) shows clearly a difference in the relative intensities between the α -pinene and $\Delta 3$ -carene experiment. Since this is a speculation and other explanations might be possible, we do not want to discuss this in the manuscript.

Comment 4: p. 17916, line 25. It is argued that only very small amounts of nitrogen containing compounds are present in the samples. However, the negative ionisation mode used for the analyses discussed here might have favoured a suppression of these compounds.

Reply: The referee is absolutely correct- the ionization method shows different sensitivity towards different species or molecules. However, we do not say that there are no nitrogen containing molecules present- we only say that we do not see a strong evidence for nitrogen containing acids in the spectrum with the applied method. To make this more clear we rewrite the passage as follows: "(2) The low signals on even m/z ratios can be attributed to ^{13}C -containing molecules since the pattern follows the odd m/z pattern and ratios to the monoisotopic ion are within the expected intensity distribution. However, the presence of nitrogen containing organic acids cannot be ruled out since the instrumental ionization method might suppress compounds with a higher gas-phase basicity."

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Comment 5: Several times in the manuscript possible artefacts of the APCI are discussed. How severe are potential cluster formation of (e.g., p.17919, line 14)? Could this partly explain the observation of high-mass compounds in the particle-phase mass spectra?

Reply: Since ambient aerosol is much more diverse, regarding inorganic and organic composition, than chamber generated aerosol, the probability of cluster formation in ambient aerosol is higher than in laboratory experiments. On the other hand, the ion trap technique stores all ions before the m/z scan. Thus, unstable clusters can dissociate in the ion-trap by collision before they are measured. How severe those effects are, cannot be answered by our dataset. Future studies are needed in order to answer this question. A promising approach regarding this question is online- high resolution mass spectrometry or the application of sensitive off-line analysis using nano-LC coupled to high resolution mass spectrometry.

Gao, Y., Hall, W. A., Johnston, M. V.: Molecular Composition of Monoterpene Secondary Organic Aerosol at Low Mass Loading, *Environ. Sci. Tech.*, 44, 7897-7902, 2010.

Hoffmann, T., Bandur, R., Hoffmann, S., Warscheid, B.: On-line characterization of gaseous and particulate organic analytes using atmospheric pressure chemical ionization mass spectrometry, *Spectrochimica Acta B*, 57, 1635-1647, 2002.

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